



# ***Interactive comment on “CO<sub>2</sub> air-sea exchange due to calcium carbonate and organic matter storage: pre-industrial and Last Glacial Maximum estimates” by A. Lerman and F. T. Mackenzie***

**Anonymous Referee #1**

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A. Lerman and F. T. Mackenzie compute with a 2 box ocean model the air-sea CO<sub>2</sub> fluxes owing to CaCO<sub>3</sub> precipitation and organic carbon production/degradation during the Last Glacial Maximum (LGM) and during pre-industrial time.

As already addressed by the other 2 referees, the manuscript is long and at times difficult to read. I strongly suggest that section 2 be shorten to essential equations and transferred to section 7 (Appendix). A careful editing is required in text and referencing.

My main concerns are:

1 - Pages 433 and 446, comparison of the “psy” factor described by Frankignoulle et al. (1994) with the “theta” factor introduced by A. Lerman and F. T. Mackenzie.

The “psy” factor is the molar ratio of CO<sub>2</sub> released to the surrounding waters (and not the CO<sub>2</sub> exchanged between the water and the atmosphere as assumed by A. Lerman

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and F. T. Mackenzie) to  $\text{CaCO}_3$  precipitation (Fankignoulle et al. 1994). The potential air-water  $\text{CO}_2$  exchange is further controlled by net ecosystem production (Gattuso et al. 1995). The actual air-water  $\text{CO}_2$  exchange will be also controlled by the water residence time (and volume of the water body) within the ecosystem and the air-water  $\text{CO}_2$  gradient of incoming seawater (Gattuso et al. 1996; Frankignoulle 1996; Bates 2002).

The “theta” factor is the ratio of  $\text{CO}_2$  released from various processes (“riverine DIC inputs”, “organic carbon respiration”, “primary production” and “ $\text{CaCO}_3$  precipitation”) to  $\text{CaCO}_3$  precipitation.

Thus, the 2 factors are conceptually different, not comparable and the attempts of comparison should be removed.

Furthermore, the “psi” factor applies to an ecosystem level (e.g. a coral reef as originally developed by Fankignoulle et al. 1994) while the “theta” factor applies to a global oceanic scale. Which brings us to the actual usefulness of such a factor, since there is a strong temporal and spatial (both vertically and horizontally) decoupling of the processes grouped in the “theta” factor. For instance, in the open ocean, primary production (in surface waters) is usually decoupled from respiration (sub-surface to intermediate waters). Degradation of river organic carbon occurs in near-shore waters (estuaries) while  $\text{CaCO}_3$  production mostly occurs in coral reefs that usually flourish in areas devoid of river inputs. The corollary of the usefulness of the “theta” factor is: what can we conclude from a two box ocean model applied to the open oceanic and coastal waters?

2 - I'm surprised how the A. Lerman and F. T. Mackenzie computed DIC and TA (and the “theta” factor). They used a constant pH of 8.35 for the LGM based on Sanyal et al. (1995), 3 different temperatures and assumed a constant  $\text{pCO}_2$  of 185 ppm to compute TA and DIC.

Firstly, a constant pH of 8.35 for the LGM is an average value that should be associated

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to a given average water temperature. From these averages and a pCO<sub>2</sub> of 185 ppm, DIC and TA should have been computed. Then from these LGM averages of DIC and TA the various parameters (pH and “theta” factor) should have been computed from the different temperatures (5, 15 and 25°C), since DIC and TA are independent from temperature unlike the other parameters (pH, “theta” and CaCO<sub>3</sub> saturation state). The approach used by the authors of a constant pH for 3 different temperatures is not only unrealistic but its usefulness difficult to apprehend.

Secondly, A. Lerman and F. T. Mackenzie state in page 440 that “In pre-industrial time, the ocean was a source of atmospheric CO<sub>2</sub> owing to heterotrophic respiration of organic matter brought by rivers from land and produced in situ, as well as owing to biological calcification in the coastal zone”. If so, pCO<sub>2</sub> in seawater must have been higher than atmospheric pCO<sub>2</sub> although the authors use the value of 185 ppm in their computations (equilibrium with the atmosphere). Also, although the whole oceanic realm (coastal waters + open ocean ; surface + deepest layers) was probably heterotrophic in pre-industrial time (assuming a steady-state imbalance between river organic inputs and final burial in sediments), there must have been a spatial heterogeneity in ecosystem metabolism: surface layers versus deeper layers ; proximal versus distal coastal areas (e.g. Rabouille et al. 2001). This brings us again to point 1 regarding the usefulness of a two box ocean model to tackle highly heterogeneous biological and chemical processes and extremely complex feedbacks between biology and climate.

In conclusion, I agree with the other referees that this manuscript requires major modifications before being acceptable for publication in Biogeosciences.

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Gattuso J-P, Pichon M, Dellesalle B, Canon C, Frankignoulle M (1996) Carbon fluxes in coral reefs. I. Lagrangian measurement of community metabolism and resulting air-sea CO<sub>2</sub> disequilibrium. *Mar Ecol Prog Ser* 145:109-121

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Rabouille C, Mackenzie FT, Ver LMB (2001) Influence of the human perturbation on carbon, nitrogen, and oxygen biogeochemical cycles in the global coastal ocean. *Geochimica et cosmochimica acta* 65:3615-3641

Sanyal, A., Hemming, G., Hansen, G, and Broecker, W. (1995) Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera, *Nature* 373: 234-237.

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Interactive comment on *Biogeosciences Discussions*, 1, 429, 2004.

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